

PATENT SPECIFICATION

779.880



Date of Application and filing Complete Specification: March 1, 1954.

No. 6001/54.

Application made in Switzerland on Feb. 27, 1953.

Application made in Switzerland on Aug. 14, 1953.

Complete Specification Published: July 24, 1957.

Index at acceptance:—Class 2(4), D1L, P1A(2A1: 2A2: 3: 4A: 4B), P1B(2: 3: 4), P1F(4: 5: 6), P9A3(B2: D1: F).

International Classification:—C09b.

COMPLETE SPECIFICATION

Functional Derivatives of Azo-Dyestuffs Containing Sulphonic Acid Groups and process for making them

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement.—

Azo dyestuffs containing sulphonic acid groups are known and available in large numbers. However, dyestuffs containing functionally converted sulphonic acid groups, especially sulphonic acid amide groups, have recently become increasingly important, and especially complex metal compounds of ortho:ortho'-dioxo-monoazo-dyestuffs of this kind. Like the dyestuffs containing sulphonic acid groups those containing sulphonic acid amide groups are prepared from diazo-components and coupling components which already contain the said groups. It will be understood that components containing sulphonic acid groups are accessible more easily or in greater numbers than those containing sulphonic acid amide groups. Similar considerations obviously also apply in the field of dyestuffs.

The present invention enables the sulphonic acid groups in ortho:ortho'-dioxo-azo-dyestuffs containing such groups to be converted into sulphonic acid amide or sulphonic acid ester groups, and thus extends the range of available dyestuffs of this kind. Moreover, the process of this invention is also advantageous for the manufacture of some of the dyestuffs of this kind available hitherto.

By the process of this invention functional derivatives of dyestuffs containing sulphonic acid groups are made by reacting an acyl derivative of an ortho:ortho'-dioxo-azo-dyestuff containing at least one sulphonic acid group in an inert solvent or diluent with a compound of pentavalent phosphorus containing at least three carbon atoms, and, if desired, converting an acid halide group in

the resulting acid halide into a sulphonic acid amide group or a sulphonic acid ester group.

The acyl derivatives serving as starting materials are advantageously prepared by acylating ortho:ortho'-dioxo-azo-dyestuffs containing sulphonic acid groups. These dyestuffs may contain one, two or more sulphonic acid groups. Especially suitable are, for example, monoazo-dyestuffs which contain two sulphonic acid groups or advantageously a single sulphonic acid group. The dyestuffs may be otherwise substituted in any desired manner. However, it is generally desirable to use dyestuffs which contain, in addition to the hydroxyl groups in ortho-position to the azo linkage, no substituents capable of reacting with phosphorus halides of the kind mentioned above, for example, further hydroxyl groups or primary amino groups, unless reaction with such substituents is desired or is at least not disadvantageous. As a substituent of this kind there may be mentioned above all the carboxylic acid group, which is converted into a carboxylic acid halide group when reacted with a phosphorus pentahalide.

The azo linkage may be bound, for example, on each side to an aryl carbon atom or on one side to an aryl carbon atom and on the other to an enolisable or enolised ketomethylene group. There may be used, for example, ortho:ortho'-dioxo-monoazo-dyestuffs of which the azo linkage is bound on one side to a benzene nucleus and on the other to a naphthalene nucleus or to a 1-phenyl-3-methyl-5-pyrazolone residue. As is known dyestuffs of this kind can be made especially easily and in large numbers by coupling an ortho-oxy-diazo-compound of the benzene series with an oxynaphthalene capable of coupling in ortho-position to the hydroxyl group or with a 1-phenyl-3-methyl-5-pyrazolone, at least one of the starting materials containing at least one sulphonic acid group. The coupling components, and 90

especially the diazo components, may contain further substituents in addition to those mentioned above. Thus, there come into consideration for example, as diazo components ortho-oxy-aminobenzenes which contain the following substituents: Nitro groups, alkyl groups such as ethyl or methyl, alkoxy groups such as ethoxy or methoxy, halogen atoms such as fluorine, bromine or especially chlorine, trifluoromethyl groups, carboxylic acid groups, aryl sulphone groups or aryloxy groups.

Apart from these monoazo-dyestuffs there may be used as starting materials other monoazo-dyestuffs corresponding to the definition given above, for example, those in which the azo linkage is bound on both sides to a naphthalene nucleus, or on one side to a naphthalene nucleus and on the other to a pyrazolone nucleus, and which can be obtained, for example, by coupling a diazotised ortho-oxy-aminonaphthalene sulphonic acid, such as 1-amino-2-oxy-naphthalene-4-sulphonic acid or 2-amino-1-oxy-naphthalene-4-sulphonic acid, with an oxynaphthalene or an oxynaphthalene sulphonic acid or a 1-phenyl-3-methyl-5-pyrazolone.

Finally, there may also be mentioned dyestuffs which are obtained by coupling an ortho-oxy-diazo compound with an oxygen-benzene capable of coupling in ortho-position to the hydroxyl group, an acetoacetylaminic compound, 2:4-dioxyquinoline or barbituric acid.

Ortho:ortho'-dioxy-azo-dyestuffs can be converted in the form of their free acids or as alkali metal salts into the acyl derivatives serving as starting materials in the process of the invention. If the dyestuffs contain more than one sulphonic acid group these groups may be present only partially in the form of alkali metal sulphonate groups. Depending on its constitution it is sometimes especially advantageous to use the dyestuff in one or other of these forms for the acylation and the subsequent reaction with the phosphorus compounds.

As the acyl groups usually serve only to protect the hydroxyl groups in ortho-position to the azo linkage during the treatment with the phosphorus compounds and they are subsequently split off, it is generally desirable to carry out the acylation with an easily accessible acylating agent or one of simple constitution. Especially advantageous in many cases are acylating agents which introduce acyl residues derived from carboxylic acids of low molecular weight, especially aliphatic carboxylic acids, such, for example, as the propionyl and especially the acetyl residue. There may be used the anhydrides or halides of such acids, for example butyric acid chloride, propionic acid chloride, acetyl chloride or acetic anhydride.

In certain cases, especially for acylating

monoazo-dyestuffs, in which the azo linkage is bound on each side to a naphthalene nucleus, it is desirable to use derivatives of aromatic carboxylic acids, especially benzoyl chloride, as the dibenzoylated compounds are more suitable for the subsequent reaction with the phosphorus halide than are, for example, the acetyl compounds.

It is in general of advantage to use the dyestuff in the dry state for the acylation and to carry out the reaction in an inert solvent or diluent. When the dyestuffs still contain water, the latter can in some cases be removed by azeotropic distillation. This method of acylation is advantageous not only because the reaction proceeds well, but is usually appropriate because the subsequent treatment is also carried out in an inert diluent and therefore in the absence of water. There is advantageously used an organic diluent; as organic diluents there come into consideration, for example, hydrocarbons such as benzene, toluene, xylenes, substituted benzenes such as nitrobenzene, monochlorobenzene, the di- and tri-chlorobenzenes liquid at room temperature, and also compounds of other kinds, such as dioxane or tertiary bases such as pyridine, or mixtures of diluents of these kinds. The acylation is advantageously carried out at a raised temperature, for example, at between about 70 and 100° C.

The acyl compounds so obtained may, if desired, be separated from the reaction mixture. However, such an intermediate separation can usually be dispensed with, and after the acylation the treatment with the phosphorus compound may be carried out in the same reaction mixture.

As compounds of pentavalent phosphorus containing at least three halogen atoms there may be used, in the present process, for example, phosphorus oxybromide or phosphorus oxychloride, but more especially a phosphorus pentahalide such as phosphorus pentabromide or advantageously phosphorus pentachloride. A phosphorus pentahalide may be used in conjunction with a phosphorus oxyhalide, in which case the latter does not serve primarily as a halogenating agent but as an inorganic diluent. When the reaction is carried out with a phosphorus oxyhalide an excess of the latter halogenating agent may serve as diluent.

Depending on the choice of the diluent and the constitution of the dyestuff the most favourable reaction temperature may vary so that in some cases, at least at the beginning of the reaction it may be desirable to cool the mixture, whereas in other cases gentle warming may be preferable after the reaction has started at room temperature. If the reaction conditions are too energetic there is a risk of side reactions taking place.

The sulphonic acid halides obtainable by the present process can be recovered from the

reaction mixture by methods in themselves known, for example, by pouring the mixture on to ice, which is recommended in the case of diluents such as dioxane which are miscible with water, and then filtering the mixture, washing the residue free from acid and drying it cautiously, for example, in vacuo at a moderately raised temperature. When the reaction mixture contains a diluent insoluble or sparingly soluble in water, it is usually of advantage, after the reaction and if desired, after allowing the mixture to cool, to filter off the resulting sulphonic acid halide, provided that the acid halide is sparingly soluble in the cold in the diluent used. When it is easily soluble and does not separate out sufficiently in the cold, it can usually be precipitated from the solution by dilution with another solvent, for example, petroleum ether. The acid halides so obtained can generally be recrystallised well from organic solvents such as benzene, chlorobenzene, nitrobenzene, ligroin, glacial acetic acid, acetone, trichloroethylene and the like, and can generally be obtained analytically pure in this manner.

In certain cases the acyl groups are so loosely bound to the hydroxyl groups that they split off even during the usual methods of working up the sulphonic acid halides.

The new acid halides are ortho'-ortho'-dioxo-azo-dyes which contain at least one sulphonic acid halide group, or acyl derivatives of these dyestuffs. They are valuable intermediate products which can be further treated, for example, in the manner hereinbefore mentioned. In general these products can be reacted by methods in themselves known with any compounds which are capable of reacting with sulphonic acid halides. Valuable products are obtained by condensing the acid chlorides, as already stated, with compounds which contain at least one —NH— group, or at least one hydroxyl group.

In addition to ammonia, there come into consideration for this condensation a very wide variety of amines, especially primary monoamines. In order to ensure a unitary course of reaction it is generally of advantage to react sulphonic acid halides, which contain more than one sulphonic acid halide group or one such group and a carboxylic acid halide group, with monoamines. For the same reason it is recommended to condense di- or polyamines with monosulphonic acid halides containing no further reactive halogen atoms.

In other respects the choice of the amine may be made in accordance with the purpose for which the product is to be used. If the sulphonic acid amide to be obtained should still possess a certain solubility in water or alkalies, as is desirable, for example, in the case of dyestuffs used for dyeing textiles, it is of advantage to use ammonia or a primary amine of low molecular weight, such as monoethylamine or monoethylamine, monoethanol-

amine or even an amine which contains a group imparting solubility in water, such as aminoacetic acid (glycocoll), N-methylaminoacetic acid, aminoethane sulphonic acid (taurine) or 1-aminobenzene-4-sulphonic acid. The presence of more than one such sulphonic acid amide group in the dyestuff molecule (see the preceding paragraph) in general also enhances solubility in water.

When the sulphonic acid amides are intended to possess an extremely low solubility in water and are to be used, for example, as pigments, it is of advantage to condense monosulphonic acid halides with amines of not too low a molecular weight, such as aniline or aminonaphthalenes. Secondary amines of this kind, for example, the arylamines mentioned above, but those in which the hydrogen atom bound to nitrogen is replaced by a methyl or ethyl group, are especially advantageous. Specially in this case also it is of advantage to condense monosulphonic acid halides with diamines in the molecular ratio 2:1, for example, cyclic diamines, and also those which contain two secondary amino groups. As examples there may be mentioned diamines of the benzene series, for example, mononuclear benzenes such as 1:4-diaminobenzene or 1:4-diamino-2:5-dialkoxybenzenes, binuclear or polynuclear benzenes such as 4:4'-diaminodiphenyl, 3:3'-dichloro- or 3:3'-dimethyl- or 3:3'-dimethoxy-4:4'-diaminodiphenyl; diamines of the benzene series in which two similarly or differently substituted benzene nuclei are linked together by a suitable bridge member, for example, by an oxygen atom, by $\text{—SO}_2\text{—}$, as in the case of 4:4'-diaminodiphenyl sulphone, by —CO— as in the case of 3:3'-diaminodiphenyl ketone, by $\text{—CH}_2\text{—}$ as in the case of 3:3'-diamino-4:4'-dichlorodiphenylmethane, or by —NH—CO— , —NH—CO—HN— , $\text{—SO}_2\text{—NH}_2\text{—}$, —CH=CH— , $\text{—CH}_2\text{—CH}_2\text{—}$, —NH— or —N=N— ; aromatic diamines of a different kind such as 2:6- or 1:5-diaminonaphthalene or 2-(4'-aminophenyl)-6-aminobenzothiazole.

The condensation of the sulphonic acid halide with the amine may be carried out in an anhydrous medium and in some cases in an aqueous medium. It generally takes place surprisingly easily even at temperatures within the boiling range of normal organic solvents such as, ethanol, benzene, acetone, toluene, monochlorobenzene, dichlorobenzene or nitrobenzene. In order to accelerate the reaction it is often desirable to use an acid-binding agent, such as sodium acetate or pyridine. When the condensation is carried out with ammonia or a monoamine, it is usually advantageous to use an excess of the base as an acid binding agent. When strongly basic amines are used in some cases hydrolysis of the —O— acyl groups takes place in addition to the reaction at the sulphonic acid halide groups.

As already stated, the acid halides may also

be condensed with compounds which contain a hydroxyl group especially a phenolic hydroxy group. As examples of such compounds there may be mentioned, in addition to phenol itself, substituted oxybenzenes, such as 4-methyl-1-oxybenzene, 4-nitro-1-oxybenzene, 4-methyl-2-nitro-1-oxybenzene, oxynaphthalenes such as 1- or 2-oxynaphthalenes and also oxydiphenyl, 3-oxydiphenylene oxide or sulphide and N-methyl-3-oxy carbazole.

In this case also a monosulphonic acid halide may be condensed with a dioxy-compound in the molecular ratio 2:1 or with a compound containing n-hydroxyl groups in the molecular ratio n:1. As examples there may be mentioned dioxybenzenes such as 1:3- or 1:4-dioxybenzene, and dioxynaphthalenes, such as 1:5- or 2:6-dioxynaphthalene.

The condensation with the oxy-compound is also advantageously carried out in an organic solvent (see above) and with the addition of an acid-binding agent.

The products of the present invention may be metallised as described and claimed in our copending Application No. 5998/54 (Serial No. 779,879).

The following Examples illustrate the invention, the parts and percentages being by weight unless otherwise stated, and the relationship of parts by weight to parts by volume being the same as that of the kilogram to the litre:—

EXAMPLE 1.

89.5 parts of the dyestuff acid, obtained by

coupling diazotised 4-chloro-2-amino-1-oxybenzene-6-sulphonic acid with 5:8-dichloro-1-oxynaphthalene, are mixed with 650 parts by volume of chlorobenzene. For the purpose of complete dehydration 150 parts by volume of liquid are distilled from the mixture. After the addition of 142 parts by volume of acetyl chloride, the mixture is maintained at 80—90°C for a period of 16 hours and is then allowed to cool. There are then added 164 parts of phosphorus pentachloride in the course of $\frac{1}{2}$ hour in small portions, and the mixture is stirred for 5 hours at room temperature. The mixture is then filtered with suction and the filter residue is dried. The diacylated sulphonic acid chloride of the dyestuff is in the form of pale yellow prisms, which melt at 210—212°C with decomposition. In a manner analogous to that described above the dyestuffs prepared by coupling the diazo-components given in Column I of the following Table with the coupling components given in Column II can be acetylated in the solvents or diluents given in Column III, and converted by means of phosphorus pentachloride into the corresponding acetylated dyestuff sulphonic acid chlorides. Columns IV and V give the times and temperatures of the reactions with phosphorus pentachloride. Column VI gives characteristic properties of the resulting sulphonic acid chlorides.

In this Table, as in all the other Tables, the reaction temperatures are those of the heating baths.

	I	II	III	IV	V	VI
1	2-amino-1-oxybenzene-4-sulphonic acid	1-phenyl-3-methyl-5-pyrazolone	Chlorobenzene	$\frac{1}{2}$ hour	50–60°C.	Yellow crystalline powder, melting at 195–196°C.
2	2-amino-4-chloro-1-oxybenzene	1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid	Chlorobenzene	3½ hours	20°C.	yellow crystalline powder, melting at 211–212°C.
3	6-nitro-1-amino-2-oxy-naphthalene-4-sulphonic acid	1-phenyl-3-methyl-5-pyrazolone	Chlorobenzene	5 hours	20°C.	yellow-red crystalline powder, melting above 250°C. with decomposition
4	4-chloro-2-amino-1-oxybenzene-6-sulphonic acid	2-oxynaphthalene	Chlorobenzene	1½ hours	20°C.	pale violet unstable product
5	2-amino-1-oxybenzene-4-sulphonic acid	1-acetoacetyl-amino-2-chlorobenzene	Chlorobenzene	20 hours	20°C.	pale yellow crystalline powder
6	2-amino-5-nitro-1-oxybenzene	1-acetoacetyl-amino-2-chlorobenzene-4-sulphonic acid	chlorobenzene	4 hours	20°C.	yellow crystalline powder
7	4-chloro-2-amino-1-oxybenzene-6-sulphonic acid	1-phenyl-3-methyl-5-pyrazolone	Benzene	20 hours	40–50°C.	orange-yellow powder precipitated by petroleum ether; melting at 204–205°C. with decomposition
8	1-amino-2-oxy-naphthalene-4-sulphonic acid	1-phenyl-3-methyl-5-pyrazolone	toluene, xylene, chlorobenzene, ortho-dichlorobenzene	3 hours	50–60°C.	brick-red crystalline powder; melting at 206–207°C. with decomposition
9	1-amino-2-oxynaphthalene-4-sulphonic acid	1-(4'-chloro)-phenyl-3-methyl-5-pyrazolone	chlorobenzene	16 hours	20°C.	brown-orange crystalline powder

Analysis by combustion shows that the products Nos. 1–3 and 5–9 probably contain one acetyl radical. Product No. 4 after some time becomes a red crystalline compound, analysis of which shows that it is an ortho: ortho'-dihydroxy-compound free from acyl groups.

EXAMPLE 2.

A mixture of 44.8 parts of the dyestuff acid, obtained by coupling diazotised 4-chloro-2-amino-1-oxybenzene-6-sulphonic acid with 5:8-dichloro-1-oxy-naphthalene, 700 parts by volume of dry chlorobenzene and 100 parts by volume of acetic anhydride is heated for 7 hours in an oil bath at 140–150°C, the mixture is then stirred until cold, the solid product is filtered off with suction, washed with benzene and dried in vacuo at 50–60°C.

The dyestuff pre-heated in this manner is pulverised, and covered with 200 parts by volume of dry chlorobenzene. After 100 parts by volume of liquid have been distilled from the mixture, 41 parts of phosphorus pentachloride are added at room temperature and the mixture is stirred for 16 hours at room temperature.

The unitary crystallite consisting of large yellow prisms is then filtered off with suction, washed with petroleum ether and dried in

vacuo. The product can be obtained in an analytically pure form by recrystallisation from benzene. Analysis by combustion shows that it is the diacetylated sulphonic acid chloride of the parent dyestuff.

In a similar manner the dyestuffs produced by coupling the diazo components given in Column I of the following Table with the coupling components given in Column II can be acetylated with acetic anhydride in the solvents or diluents given in Column III, and then converted into the corresponding acetylated dyestuff sulphonic acid chlorides by means of phosphorus pentachloride in the solvents or diluents given in Column V. In Column IV are given the times and temperatures of the acetylations, and in Column VI the times and temperatures of the reaction with phosphorus pentachloride. Column VII gives characteristic properties of the corresponding sulphonic acid chlorides.

	I	II	III	IV	V	VI	VII
1	4-chloro-2-amino-1-oxybenzene	1-oxy-naphthalene-4-sulphonic acid	a total of 150 parts of acetic anhydride	2½ hours at 140–150°C.	Chlorobenzene	4½ hours at 20°C.	orange crystalline powder
2	4-chloro-2-amino-1-oxybenzene	1-oxy-naphthalene-5-sulphonic acid	a total of 200 parts of acetic anhydride	1/3 hour at 140–150°C.	Chlorobenzene	16 hours at 20°C.	yellow-brown crystalline powder
3	1-amino-2-oxy-naphthalene-4-sulphonic acid	1-aceto-acetyl-amino-2-chlorobenzene	200 parts of glacial acetic acid	2 hours at 130–150°C.	Chlorobenzene	16 hours at 20°C.	yellow crystalline powder
4	1-amino-2-oxy-naphthalene-4-sulphonic acid	1-(2'-chloro)-phenyl-3-methyl-5-pyrazolone	a total of 100 parts of acetic anhydride	1/3 hour at 160–170°C.	Dioxane	16 hours at 20°C.	Yellow-orange crystalline powder

Analysis by combustion shows that the products Nos. 1 and 2 are probably diacetylated and Nos. 3 and 4 probably monoacetylated ortho:ortho'-dihydroxy-azo-dyestuffs.

EXAMPLE 3.

39.4 parts of the dyestuff acid, obtained by coupling diazotised 1-amino-2-oxy-naphthalene-4-sulphonic acid with 2-oxy-naphthalene, are introduced in a well dried condition into 200 parts by volume of dry pyridine. 35 parts by volume of benzoyl chloride are introduced dropwise in the course of 20 minutes, the mixture is heated for 2 hours at 40–50°C.

and then allowed to cool. The mixture is then filtered with suction and the residual solid product consisting of small pale yellow needles is washed with dilute hydrochloric acid. The pale straw yellow product is dried in vacuo at 70–80°C.

31 parts of the dyestuff pre-treated in this manner in 130 parts by volume of chlorobenzene are mixed in the course of ½ hour in portions with 22 parts of phosphorus pentachloride. After stirring the mixture for 3 to 4 hours at room temperature, it is filtered and the uniform residue consisting of small slightly

curved pale yellow needles is washed with petroleum ether and dried. The resulting diacylated sulphonic acid chloride can be freed from adherent impurities of acid reaction by treatment with water.

Instead of 35 parts by volume of benzoylchloride there may be used with the same good result 52.5 parts of para-chlorobenzoyl chloride.

Instead of chlorobenzene there may be used as diluent or solvent toluene, benzene, or xylene.

The dyestuffs prepared by coupling the diazo components given in Column I of the following Table with the coupling components

given in Column II can be benzoylated with benzoyl chloride in pyridine in a similar manner, and then converted into the corresponding benzoylated dyestuffs sulphonic acid chlorides with phosphorus pentachloride in the solvent or diluents mentioned in Column IV. In Column III are given the times and temperatures of the acylation and in Column V the times and temperatures of the reactions with phosphorus pentachloride, and Column VI gives characteristic properties of the final products.

	I	II	III	IV	V	VI
1	4-chloro-2-amino-1-oxybenzene	2-oxynaphthalene-6-sulphonic acid	1 hour 60-70°C.	Chlorobenzene	1 hour 20°C.	pale orange powder
2	4-nitro-2-amino-1-oxybenzene-6-sulphonic acid	2-oxynaphthalene	1 hour 60-70°C.	Chlorobenzene	18 hours 20°C.	dark orange powder
3	4-chloro-2-amino-1-oxybenzene	1-oxynaphthalene-4-sulphonic acid	4 hours 60-70°C.	benzene	5 hours 20°C.	yellow powder
4	2-amino-1-oxybenzene-4-sulphonic acid	2-oxynaphthalene	3 hours 50-60°C.	Chlorobenzene	1 hour 20°C.	pale orange powder
5	1-amino-2-oxynaphthalene-4-sulphonic acid	1-acetoacetyl-amino-2-chlorobenzene	Add benzoyl chloride	Chlorobenzene	2 hours 20°C.	yellow crystalline powder
6	1-amino-2-oxy-6-nitronaphthalene-4-sulphonic acid	2-oxynaphthalene	2 hours 40-50°C.	Chlorobenzene	16 hours 20°C.	ochre yellow powder

The benzoylated products must be isolated by pouring the pyridine solution on to a mixture of ice and hydrochloric acid.

Analysis by combustion shows that Nos. 2, 3, 4 and 6 probably contain two benzoyl groups and No. 5 probably contains one benzoyl group.

EXAMPLE 4.

27.9 parts of the dyestuff sulphonic acid chloride described in Example 3 are introduced into 100 parts by volume of chlorobenzene at 80-90°C. A stream of dry ammonia gas is passed over the mixture for 3 hours. After cooling the mixture, the solid material is filtered off with suction and dried. It is first washed with hot water, and, in order

to complete the splitting off of the benzoyl groups, it is dissolved in hot alcohol with the addition of a sodium hydroxide solution of 35 per cent strength and reprecipitated from the solution by the addition of hydrochloric acid of 30 per cent strength and, finally washed with a hot very dilute solution of hydrochloric acid. The dyestuff sulphonamide obtained in this manner is a claret coloured powder.

The acylated dyestuff sulphonic acid chlorides given in Column I of the following Table can be converted in a similar manner into the corresponding dyestuff sulphonic acid amides in the solvents or suspension media given in Column II by means of the amidating agents given in Column III. Column IV gives characteristic properties of the final products.

	I	II	III	IV
1	Chloride of No. 1 in the Table in Example 1	Benzene	gaseous ammonia	Brownish powder
2	Chloride of No. 3 in the Table in Example 1	Benzene	gaseous ammonia	Claret coloured powder
3	Chloride of No. 4 in the Table in Example 1	Benzene	gaseous ammonia	Red-brown powder
4	Chloride of Example 1	ethanol	aqueous ammonia of 25% strength	Claret coloured powder
5	Chloride of No. 8 in the Table in Example 1	Benzene	gaseous ammonia	Red-orange powder

EXAMPLE 5.

- 14.5 parts of the dyestuff sulphonic acid chloride No. 8 in the Table in Example 1 are mixed in 100 parts by volume of alcohol with 6.1 parts by volume of morpholine, and the mixture is heated in a water bath for one hour at 80–90°C. After cooling the mixture, it is filtered with suction, the filter residue is washed with hot water, and for the purpose of further purification the product is dissolved in hot alcohol by the addition of a concentrated aqueous solution of sodium hydroxide, and reprecipitated with concentrated aqueous hydrochloric acid, then filtered off with suction and washed free from acid with hot water.

When dried the sulphonic acid morpholide is a bright scarlet powder and can be obtained in analytically pure form by recrystallisation from chlorobenzene. It melts at 246–247°C with decomposition.

In a corresponding manner the acylated dyestuff sulphonic acid chlorides given in Column I of the following Table can be reacted in the solvents or suspension media given in Column II with the compounds given in Column III. Column IV gives the conditions of time and temperature used in carrying out these reactions. Column V gives characteristic properties of the final products.

	I	II	III	IV	V
1	Chloride of No. 4 of the Table in Example 1	Ethanol	Morpholine	1 hour at 80–90°C.	brown-red powder, melting above 250°C, with decomposition
2	Chloride of Example 1	Ethanol	Morpholine	1 hour at 80–90°C.	brick red powder
3	Chloride of Example 1	Benzene	Mono-methyl-aniline, pyridine	4½ hours at 80–90°C.	claret coloured powder
4	Chloride of No. 8 of the Table in Example 1	—	Dimethyl-amine of 20% strength	1 hour at 80–90°C.	red powder
5	Chloride of No. 8 of the Table in Example 1	Ethanol	Isopropyl-amine of 50% strength	2 hours at 80–90°C.	red powder

	I	II	III	IV	V
6	Chloride of No. 8 of the Table in Example 1	Benzene	Aniline	1 hour at 80-90°C.	red crystalline powder
7	Chloride of No. 8 of the Table in Example 1	Benzene	1-Amino-4-methoxybenzene	5 hours at 80-90°C.	brown-red powder
8	Chloride of No. 5 of the Table in Example 1	Water	Mopholine	1/3 hour at 100-110°C.	yellow powder
9	Chloride of No. 1 of the Table in Example 3	Ethanol	Methylamine of 30% strength	2/3 hour at 80-90°C.	red powder
10	Chloride of No. 2 of the Table in Example 3	—	Dimethylamine of 33% strength	4 hours at 50-60°C. then 3 hours at 80-90°C.	brown orange powder
11	Chloride of No. 3 of the Table in Example 3	Benzene	1-Amino-2-methoxybenzene	6 hours at 80-90°C.	claret coloured crystalline powder with a bronze lustre
12	Chloride of No. 1 of the Table in Example 2	—	Methylamine of 30% strength	2 hours at 80-90°C.	dark red powder
13	Chloride of No. 2 of the Table in Example 2	Benzene	Mopholine	1/2 hour at 80-90°C.	claret coloured powder
14	Chloride of No. 4 of the Table in Example 3	Benzene	Aniline	6 hours at 80-90°C.	yellow-red powder
15	Chloride of No. 3 of the Table in Example 2	Benzene	Mopholine	1 1/2 hours at 80-90°C.	yellow powder
16	Chloride of No. 9 of the Table in Example 1	Benzene	1-Amino-4-ethoxybenzene	5 hours at 80-90°C.	dark-red powder
17	Chloride of No. 4 of the Table in Example 2	Benzene	Aniline	6 hours at 80-90°C.	blue-red powder

	I	II	III	IV	V
18	Chloride of Example 3	—	Dimethylamine of 30% strength	3 hours at 20° C. then $\frac{1}{2}$ hour at 80–90° C.	claret coloured powder
19	Chloride of No. 6 of the Table in Example 3	Benzene	Methylamine of 30% strength	2 hours at 70–80° C.	dark green crystalline powder with bronze lustre
20	Chloride of No. 6 of the Table in Example 3	—	Dimethylamine of 30% strength	1 hour at 80–90° C.	black crystalline powder with bronze lustre

EXAMPLE 6.

To a thick paste of 23 parts of the dyestuff obtained by coupling diazotised 1-amino-2-oxynaphthalene-4-sulphonic acid with 1-acetoacetylaminio-2-chlorobenzene in 150 parts by volume of pyridine there are poured 19.3 parts by volume of benzene-sulphochloride, whereby after rapid dissolution of the dyestuff while the mixture heats up spontaneously to about 40° C. rhombic crystals crystallise out. The crystallisate is separated by filtration after the mixture has cooled, treated with dilute hydrochloric acid and then washed completely free from acid and salt with cold water. After drying in vacuo at 50–60° C. there are obtained 20 parts of the sulphacylated starting dyestuff in the form of brilliant gold yellow crystal powder.

18.1 parts of this pretreated dyestuff are suspended in 75 parts by volume of chlorobenzene and mixed with 12.5 parts of phosphorus pentachloride with water cooling. After stirring for 3 hours with water cooling, the product consisting of prismatic needles is filtered, washed with petroleum ether, dried in vacuo at room temperature, treated with cold water to remove any by-products having an acid reaction and then dried again. There are obtained 14.3 parts of yellow crystal powder which is the sulphacylated sulphonic acid chloride of the starting dyestuff. The product can be recrystallised from toluene or a similar solvent.

If instead of 19.3 parts by volume of benzene-sulphochloride 11.5 parts by volume of methane sulphochloride are used and the same process carried out as described above, there are obtained 17.6 parts of the corresponding derivative as a yellow crystal powder.

EXAMPLE 7.

21.2 parts of the dyestuff obtained by coupling diazotised 1-amino-2-oxynaphthalene-4-sulphonic acid with 1-phenyl-3-methyl-5-pyrazolone are treated as described in Example 6

with methane sulphochloride in pyridine, then with phosphorus pentachloride in chlorobenzene. There are obtained 17.5 parts of the sulphacylated sulphonic acid chloride of the starting dyestuff as a brilliant orange powder which crystallises from toluene in the form of orange yellow clusters of needles.

What we claim is:—

1. A process for the manufacture of functional derivatives of azo-dyestuffs containing sulphonic acid groups, wherein an acyl derivative of an ortho:ortho'-dioxo-azo-dyestuff containing at least one sulphonic acid group is reacted in an inert solvent or diluent with a compound of pentavalent phosphorus containing at least three halogen atoms.

2. A process as claimed in claim 1, wherein an acyl derivative of an ortho:ortho'-dioxo-monoazo-dyestuff containing at least one sulphonic acid group is used as starting material.

3. A process as claimed in claim 1 or 2, wherein the acyl-compound used as starting material is derived from a carboxylic acid.

4. A process as claimed in claim 1, 2 or 3, wherein the acyl-compound is an acetyl or benzoyl compound.

5. A process as claimed in any one of claims 1–4, wherein a phosphorus penta-halide advantageously phosphorus penta-bromide or penta-chloride is used as the phosphorus compound.

6. A process as claimed in any one of claims 1–5, wherein the treatment with the phosphorus compound is carried out in an organic diluent.

7. A process as claimed in any one of claims 1–6, wherein an acid halide group in the acid halide so obtained is converted into a sulphonic acid ester group.

8. A process as claimed in any one of claims 1–6, wherein an acid halide group in the acid halide so obtained is converted into a sulphonic acid amide group.

9. A process as claimed in claim 8, wherein the acid halide is reacted with ammonia or a primary or secondary monamine.
- 5 10. A process as claimed in any one of claims 1—9, wherein there is used as starting material an O-royl compound of an ortho: ortho'-dioxy-azo-dyestuff of which the azo linkage is bound on each side to a naphthalene nucleus.
- 10 11. A process as claimed in claim 10, wherein a di-O-royl compound is used as starting material.
- 15 12. A process as claimed in claim 11, in which a di-O-benzoyl compound is used as starting material.
13. A process for the manufacture of a functional derivative of an azo-dyestuff containing a sulphonic acid group conducted substantially as described in any one of the Examples or with reference to the Tables herein.
- 20 14. Ortho: ortho'-dioxy-azo-dyestuffs which contain at least one sulphonic acid halide group and acyl derivatives of such dyestuffs.
- 25 15. Ortho: ortho'-dioxy-monoazo-dyestuffs which contain at least one sulphonic acid halide group or ortho: ortho'-acyl derivatives of such dyestuffs.
16. Acyl derivatives as claimed in claims 14 or 15, in which the acyl groups are those of carboxylic acids.
17. Acyl derivatives as claimed in claim 16, in which the acyl groups are acetyl or benzoyl groups.
18. Acyl derivatives as claimed in claim 15, in which the acyl groups are those of aromatic acids, advantageously benzoic acid, and the azo linkage is bound on each side to a naphthalene nucleus.
19. Acyl derivatives as claimed in claim 18, which are diaroylated.
20. Dyestuffs or acyl derivatives as claimed in any one of claims 14—19, which contain sulphonic acid chloride groups.
21. Any one of the ortho: ortho'-dioxy-azo-dyestuffs containing at least one sulphonic acid halide group and acyl derivatives of such dyestuffs described in the Examples and Tables herein.
- 30
- 35
- 40
- 45

ABEL & IMRAY,
Agents for the Applicants,
Quality House, Quality Court,
Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1967.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.